amendments to claims 1 and 27. The remarks in support of patentability are based on the claims as amended.

Faigen U.S. Patent No. 3,912,548 discloses certain coating forming polymers combined with zirconium compounds as overcoats on chromium and /or phosphate metal conversion coatings.

In the present specification, on page 19, line 12+, Applicants teach "The aqueous protective coating component can also include conventional additives known to be useful in adhesive compositions, such as metal oxides that can include zinc oxide, magnesium oxide, lead oxide, iron oxide, cadmium oxide, zirconium oxide and calcium oxide, with zinc oxide and magnesium oxide being preferred. Another useful ingredient is mica."

The use of pigment additives like zirconium oxide as representative of many metal oxides mentioned in this passage is conventional practice. These metal oxides are not in any way recognized as an element of claims 1 and 27. Zirconium compounds are not blister suppressing agents, as shown below.

The invention resides in a general aspect of a two part metal protection that solves a problem relating to blister formation. A two-part coating system was invented whereby in the second coating, an oxidizer ("blister suppressing agent") is present. These agents are observed to suppress blister formation which occurs at the metal surface, and within the first coating. Applicants believe the agents migrate towards the metal surface from the second coating and reduce or eliminate blisters forming from released hydrogen. The invention is particularly effective where metal conversion in the underlying coating is incomplete at the time a second protective coating is applied.

Applicants provide two types of metal conversion coatings. In conjunction with the second protective coating, namely, inorganic types akin to the chromium and phosphate types disclosed in the Faigen patent, and organic types which are not disclosed in Faigen.

Independent Claims 1 and 27 (and 46) are amended to recite that the aqueous metal treatment conversion coating contains "acid and a- , an accelerator, and an organic coating forming component ". Claims 1 and 27 are novel on this basis alone over the Faigen patent.

In a second aspect of novelty, Applicants independent claims 1 and 27 recite the protective coating applied over the conversion coating contains a mixture of a blister suppressing agent and an organic film forming protective component. The blister suppressing agents are described in the text on page 16, et seq. Whereas, Faigen discloses as the second coating over inorganic conversion coatings, a mixture of a coating forming polymer with a zirconium compound, being one or more forms of ZrO_2, such as zinc carbonates. Zirconium is a Group IVB metal, and the oxidation state of the materials disclosed in Faigen is 4. Therefore zirconium compounds contemplated by the Faigen patent exhibit no re-dox potential, and do not oxidize hydrogen. See the attached Supplier technical bulletin 117, entitled *The Use of Zirconium Coatings in Surface Coatings,* by Dr. P. Moles. This report describes products representative of the zirconium compounds taught by Faigen and would be understood by the ordinary skilled person as exhibiting no re-dox potential. Therefore no blister suppressing function is available and the conclusion is inescapable that the zirconium compounds relating to Faigen are not blister suppressing agents, but rather, in Faigen are intended for insolubilizing carboxylated polymers, such as polyacrylic acid polymers, and promoting their adhesion to metal, or for providing metal sealing properties. Such uses are explained in the cited article.

Therefore, the Faigen patent does not teach or suggest an acid, accelerator and organic coating forming component in a metal conversion coating nor does the Faigen patent disclose, teach or suggest the use of a blister suppressing agent in a second protective coating. Removal of the rejection under 35, U.S.C. 102(b) is respectfully requested.

Claims 1-4, 8, 9, 11, 13-30, 32, 35-45, and 47 are in condition for allowance as no other rejections are lodged against these claims, and the dependent claims among these depend from patentably distinguished claims.

Section 103 Claim Rejections

In Paragraph 7 of the Office Action the Examiner rejected claims 5-7, 10, 31, and 33-34 under 35 U.S.C. §103(a) as being unpatentable over Faigen in view of Wimmer et al. U.S. Patent 6,235,836.

The following is taken from page 16 line 10: " The inventor has found that by including a blister suppressing agent, such as an oxidizing agent, in the subsequently applied protective coating, the blister suppressing agent in the protective coating, can diffuse to the surface of the metal and oxidize the formed hydrogen, thus reducing or even eliminating blister formation. The presence of the blister suppressing agent in the protective coating, allows the use of low levels or even no levels of accelerator in the metal treatment conversion coating component. "

Wimmer et al teach the use of zirconate or titanates in a similar stable oxidation state as $M(OR_4)$, as the zirconate carbonates disclosed in Faigen, and these are known in the art as coupling agents, or chelating agents. These compounds are not oxidizers, but interact with active hydrogen-containing polymers and surfaces upon hydrolysis. Hydrolysis does not result in any oxidizing form for zirconium or titanium compounds, hence these will not suppress blisters. These additives are used in Wimmer et al for the

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above conventional properties.

A combination of the teachings of Wimmer, et al with Faigen does not result in the claimed two part protection composition, for the reasons mentioned above in respect to undisclosed organic coating forming component and the presence of blister suppressing agent in the protective coating. Substitution of the phenolic resins of Wimmer does not give rise to compositions containing all elements as claimed, nor is such a substitution of organic resins suggestive to lead or motivate one of ordinary skill to modify the Faigen coating system to resemble the instant claims. The problem of blister suppression is not touched upon in any of the references to provide a scintilla of a teaching in a direction toward the problem, *a fortiori,* the solution provided in the claimed invention, therefore the rejection under 35 U.S.C. 103(a) of claims 5-7, 10, 31, and 33-34 which ultimately depend from claims which have been patentably distinguished must fall.

In Paragraph 8 of the Office Action the Examiner rejected claims 12 and 36 under 35 U.S.C. §103(a) as being unpatentable over Faigen in view of Beiersdorf et al. U.S. Patent 6,440,231 or Roland et al. U.S. patent 5,792,283. With respect to Beiersdorf et al, phosphate pretreatments are akin to Faigen, and followed by application of adhesives (primer/covercoats) and Roland et al teach phosphating treatments with accelerators which is also convention. Hydroxyl amine is a well-known accelerator used in many metal treatments. The combination of either secondary reference with Faigen still results in a two-part coating of an inorganic phosphate first coat, and a second coating missing still a blister suppressing agent. The combination of hydroxyl amine of Beiersdorf et al or Roland et al would not overcome the absence of elements in the conversion coating and the protective coating, therefore does not reconstruct all of the elements of the claimed invention so the rejection under 35 U.S. C. 103(a) of claims 12 and 36 is overcome with respect to the amended claims that 12 and 36 ultimately depend from.
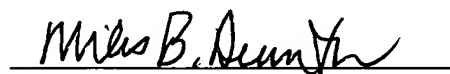
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In Paragraph 9 of the Office Action the Examiner rejected claims 46-48 under 35 U.S.C. §103(a) as being unpatentable over Beiersdorf et al. in view of Faigen. Claim 46 has been amended to recite that the conversion coating forming component comprises acid, accelerator and organic coating forming component. Neither Beiersdorf nor Faigen teach or suggest such conversion coatings, and nothing in these references provides any basis under the obviousness standard to adequately reconstruct the claimed invention.

Miscellaneous

Examiner is authorized to charge deposit account 12-2143 the amount required for a three-month extension of time for filing a response to the Office Action.

In light of the amendments and Remarks herein, Applicant submits that claims 1-48 as amended are in condition for allowance. Reconsideration and withdrawal of the claim rejections and allowance of the amended claims 1-48 are respectfully requested.
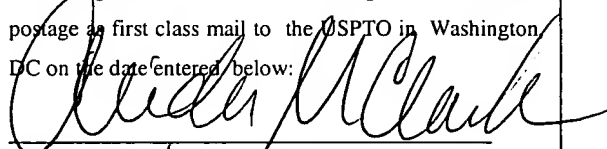
Respectfully submitted,

Miles B. Dearth

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Attorney for Applicant
Reg. No. 35,115
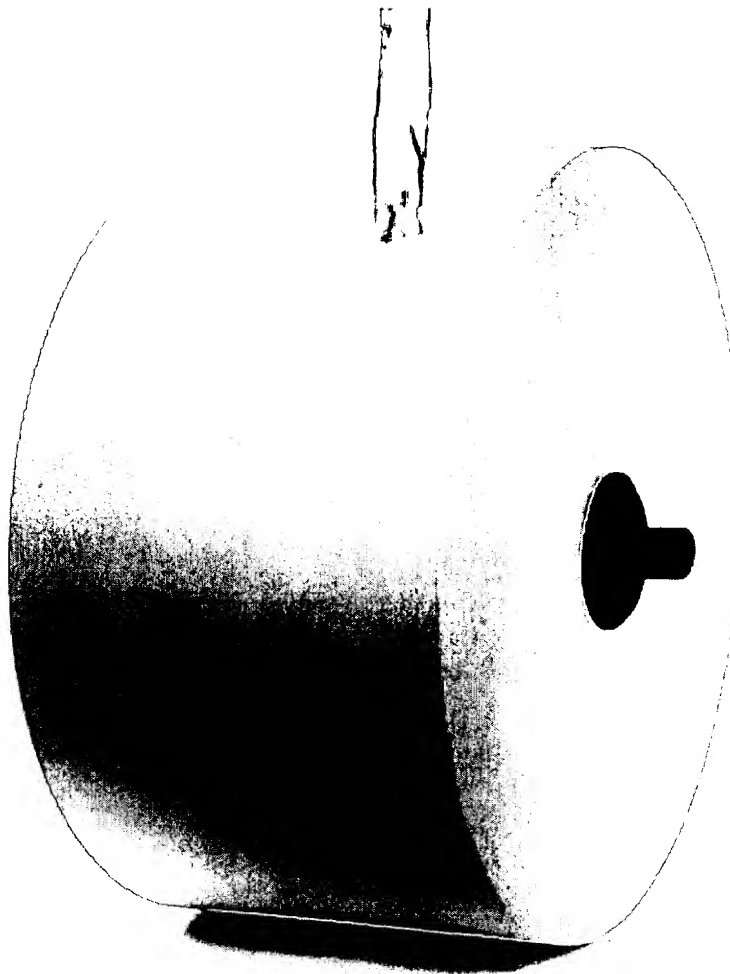919-468-5979 ext. 6204
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The Use of Zirconium in Surface Coatings

Dr Peter J Moles, MEL CHEMICALS

INTRODUCTION

Surface coatings is a wide, diverse field covering a multitude of different systems. However, there is a basic concept binding all these areas together; that coatings are applied to substrates by various means to provide protection and/or decoration. Depending on the means of application and thickness, the coating is further classified as paints, inks, etc.

This paper will show how zirconium can be used to improve properties of surface coatings in specific high usage areas. In particular it will concentrate on the use of zirconium in inks and to a lesser extent, paints.

In both inks and paints there has been movement away from long established systems. Traditionally, inks have been based on solvent soluble resins, but legislation in the USA and Europe has led to the adoption of a range of water based systems destined for use on a variety of substrates.

A slightly different situation exists in relation to paints. There has been trend away from solvent to water based systems, but high solids systems have also had an impact.

What problems are presented by these changes? As coatings become more sophisticated, demands upon them increase. An increasing number of requirements of the final coating is also called for.

Major problems found with today's surface coatings include adhesion, heat resistance, scrub resistance and water/solvent resistance.

These can be considered in turn:

(i) **ADHESION**
Getting a coating to adhere firmly to a substrate depends on a variety of effects. The polarity of the substrate surface and the polarity of the resins in the coating is of major importance.

(ii) **HEAT RESISTANCE**
The ability of a coating (especially an ink) to withstand heat and pressure is now of major importance and the ability of the resins to cope is becoming more important.

(iii) **SCRUB AND WATER/SOLVENT RESISTANCE**
Making sure the coating can survive abrasion and exposure to water/solvents is of major importance and is dependent on the thermoplastic nature of the coating.

It is now clear these problems can be overcome by the use of additives which modify certain properties of the coating. Zirconium chemicals are particularly useful for this purpose.

Adhesion can be improved by using zirconium based adhesion promoters which act as a keying agent between the body of the coating and the substrate.

Resistance to heat, scrubbing, water/solvents can also be improved by using zirconium compounds to crosslink the resins, making the resin (and hence the body of the coating) behave in a better fashion.

Before embarking on a discussion of how zirconium can be used in inks and paints, its fundamental chemistry needs to be examined.

THE CHEMISTRY OF ZIRCONIUM

Several authoritative reviews exist on zirconium chemistry and attention is drawn to those of Clearfield[1] and Farnworth, Jones and McAlpine.[2] As we are dealing primarily with aqueous systems, we will mainly confine our considerations to the aqueous solution chemistry of zirconium.
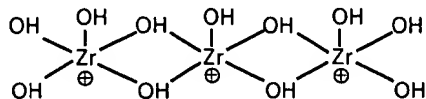
Zirconium is not a rare element, it ranks 20th in abundance in the earth's crust. It lies in Group IVB of the periodic table. The preferred oxidation state is 4 and no redox chemistry is known under these conditions, and due to a high charge to radius ratio, no stereochemical preferences are displayed. The high ratio results in hydrolysis and polymer formation, as exemplified by zirconium oxychloride which is present, in the crystal and initially on dissolution in water, as a tetrameric unit, where the four zirconium atoms are linked by hydroxyl groups. Hydrolytic polymerisation of these tetramers can be achieved by ageing, heating or by a reduction in acidity. In this case the zirconium is considered to be in a cationic polymeric species.

Similar structures are found for zirconium hydroxychloride and oxychloride, both of which are stable, acidic solutions.
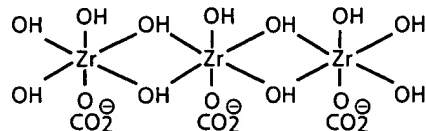
Similar polymeric structures are found in other aqueous zirconium compounds. Ammonium zirconium carbonate (AZC) is an alkaline solution containing anionic zirconium species with bridging hydroxyl groups with carbonate groups bonded to the zirconium. Where hydrolytic stability is important, partial replacement of the carbonate by chelating ligands such as tartrate ions can lead to improvements.

Zircon sand - the raw material for all zirconium chemicals

Zirconium orthosulphate also exists as an anionic species (as shown in Fig 1) but is acidic in nature. Zirconium acetate is again a polymeric material but in this case the exact structure in solution is not known with certainty, although it is believed to be a neutral polymeric species as shown in Fig 1. It is interesting to note that zirconium acetate can impart water repellancy to a substrate on drying after treatment. It is postulated that the acetate groups are held, by virtue of the polymeric nature of the zirconium, in positions which inhibit water penetration. Solvent soluble zirconium compounds (normally carboxylates) have a similar polymeric structure, containing bridging hydroxyl groups.

With these species the possibility exists of the carboxylates acting as bridging (bidentate) as well as monodentate ligands as shown in fig 2. Solvent solubility is a function of the carboxylate and different carboxylates exhibit solubilities in organic solvents. From a toxicity point of view, zirconium is not regarded with suspicion. Ammonium zirconium carbonate has FDA and BfR approval for use as a component of paper and paperboard in contact in food. Zirconium compounds are widely used as driers in the paint industry as replacements for toxic lead systems.

Fig 1. Useful structural representations of polymeric zirconium species
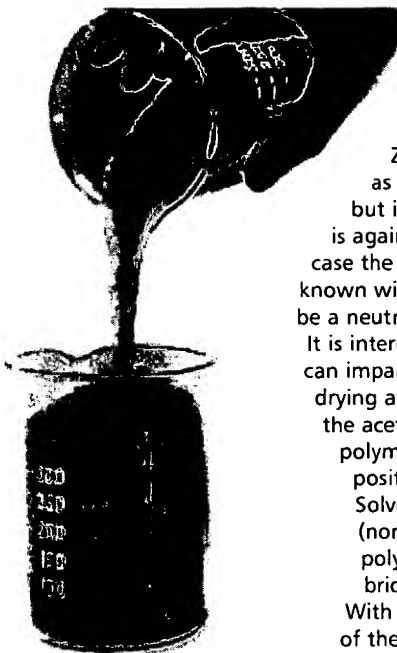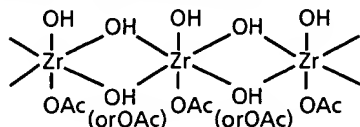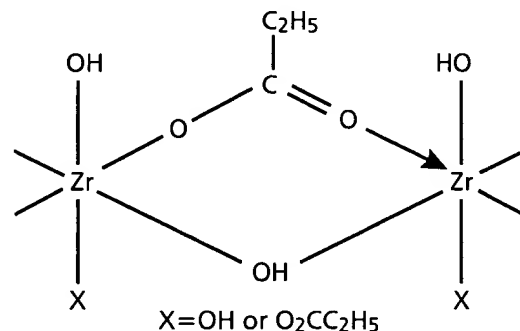
CATIONIC - zirconium oxychloride
- zirconium hydroxychloride

ANIONIC - ammonium zirconium carbonate
- zirconium orthosulphate

NEUTRAL - zirconium acetate

Fig 2. Zirconium Propionate

$X = OH$ or $O_2CC_2H_5$

As we have seen, zirconium compounds exist in aqueous and solvent solution as polymeric species, the exact nature of these polymeric species depends on the chemical composition and mode of preparation.

These polymeric species of zirconium can interact with functional groups on organic polymers. It is known that zirconium reacts strongly with carboxyl groups forming strong bonds whilst hydrogen bonds are formed with hydroxyl groups, which can range from quite weak to fairly strong interactions. These points are clearly illustrated in Figs 3 and 4 using ammonium zirconium carbonate (AZC) as the source of Zr.

It is possible to vary the chain length of the zirconium species by altering temperature, pH and chelating agents and this can have a significant effect on the crosslinking reaction.

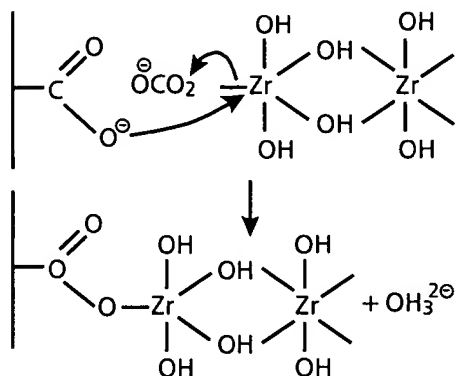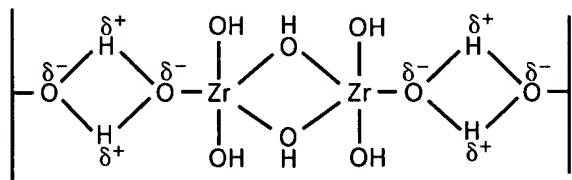## Fig 3. Interaction of AZC with carboxylated polymers

Fig 4. Interaction of AZC with hydroxylic polymer solutions

THE APPLICATION OF ZIRCONIUM IN PAINTS AND INKS

1. EXISTING APPLICATIONS

Zirconium compounds currently find use in solvent based paint as co-ordination driers where zirconium carboxylates can be used in place of toxic lead driers and in water based paints as thixotropes. Zirconium compounds are also used in metal treatment where zirconium fluorides improve the adhesion of coatings aluminium metals. However it is not intended to review these existing areas in any great detail, rather it is intended to look towards the newer application areas.

2. SOLVENT BASED INKS

(a) Adhesion promotion

The standard adhesion promoter was titanium acetylacetonate but zirconium propionate is now used as an adhesion promoter in flexographic and gravure inks to improve adhesion to difficult substrates. The standard inks used in Europe are normally based on nitrocellulose resins, often in combination with urethanes.

The efficiency of zirconium propionate as an adhesion promoter in these types of inks is demonstrated in the following work. A much simplified nitrocellulose ink was used in the study and zirconium propionate was compared to titanium acetylacetonate, as detailed in the formulation below:

Nitrocellulose resin	20 parts
Pigment	5 parts
Ethylacetate	50 parts
Ethanol	50 parts
Adhesion promoter	0 - 2 parts

Printing the inks on to treated polypropylene and testing the adhesion by means of the tape test shows how effective zirconium propionate is as an adhesion promoter. (See Fig 5.) Dissolution of the zirconium propionate in ethylacetate to give a 30 - 50% w/w solution and adding to the nitrocellulose varnish is the best method of introducing Zr.

Fig 5. Adhesion tape tests of adhesion promoters Titanium Acetylacetonate and Zirconium Propionate
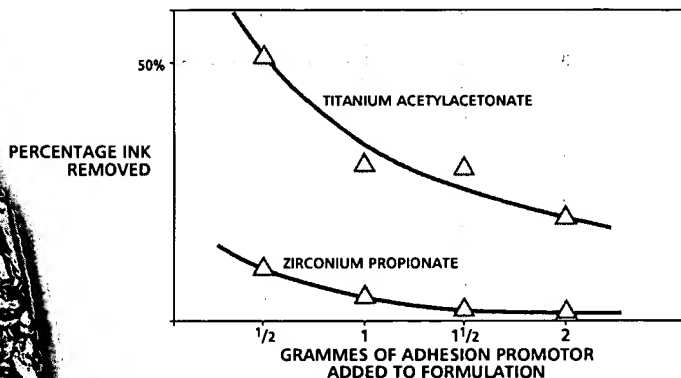
A typical nitrocellulose-urethane ink in which zirconium propionate can be used to major effect is shown below.

Nitrocellulose	18 parts
Urethane	20 parts
Dibutylphthalate	14 parts
Ethanol	6-8 parts
Ethylacetate	34 parts
Pigments	5 parts
Zirconium propionate	1 - 3 parts

Other types of ink commonly used in flexographic and gravure printing are based on cellulose acetate propionate (CAP). Again zirconium propionate can be used to improve the adhesion, a typical formulation is given below:

Typical white base ink

Cap Resin	8.73
Plexigum	4.37
Dibutylphthalate	1.75
TiO_2	26.20
Zirconium propionate	1.31
1 : 1 Industrial Ethanol:	
Ethyl acetate	57.64

Excellent adhesion and heat resistance is achieved. Obviously zirconium propionate works, but what is the mechanism? A typical packaging film is corona discharge-treated polypropylene. The discharge treatment lowers surface tension and so allows wetting and hence printing. However, on a molecular level this lowering of the surface tension is achieved by forming functional groups on the surface (i.e. surface oxidation).

The groups commonly found are carboxyl, carbonyl, hydroxyl and amido. In the absence of any adhesion promoters these functional groups interact via hydrogen bonds with the inks resins to give some mild improvement in adhesion. The mechanism of action of zirconium adhesion promoters is quite straightforward. Oxygenated species on the surface of the plastic interact strongly with Zr which can also bond firmly to the ink resin, allowing the formation of a covalently bonded system which greatly enhances the adhesion. The zirconium also crosslinks the nitrocellulose resins at the same time, improving physical properties such as heat and scrub resistance. (See Fig 6.)

(b) Heat and scrub resistance

As well as improving the adhesion, zirconium propionate also improves the heat resistance of ink films. A typical nitrocellulose or CAP ink will show improvements in heat resistance as well as adhesion. It is however with polyamide inks that heat resistance becomes important. These inks, although showing excellent adhesion, usually display very poor heat resistance. This problem can be overcome by using zirconium compounds in combination with nitrocellulose resins. A typical formulation is as follows.

Polyamide resin	23 parts
Nitrocellulose resin	3 parts
Toluene	12 parts
Isopropylacetate	10 parts
n-propylalcohol	20 parts
iso-propylalcohol	17 - 20 parts
Pigment	12 parts
Adhesion promoter	0-3 parts

The zirconium works because it crosslinks the nitrocellulose, effectively increasing the molecular weight and allowing the dissipation of heat applied in a sealing process.

(c) General comments

The viscosity of zirconium containing inks can be easily controlled by use of maleic resins. As will be understood by now, these resins contain groups which can chelate the zirconium and this chelation stops premature reaction with the ink resins. Maleic resins of low acid number are recommended, as suggested below:

Nitrocellulose resin	20 parts
Pigments	5 parts
Ethylacetate	50 parts
Ethanol	50 parts
Maleic resin	1 - 5 parts
Zirconium propionate	1 - 3 parts

As well as improvements in viscosity, one can also (under certain circumstances) see better adhesion and heat resistance.

Pigment stability is very good, with zirconium compounds displaying no adverse reaction with a standard range of pigments.

Fig 6. *Interaction of Zr chemicals with polyolefin surfaces*
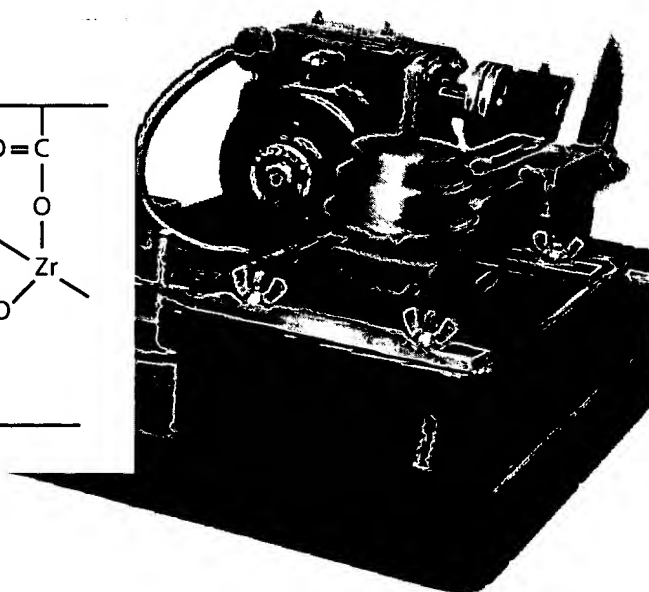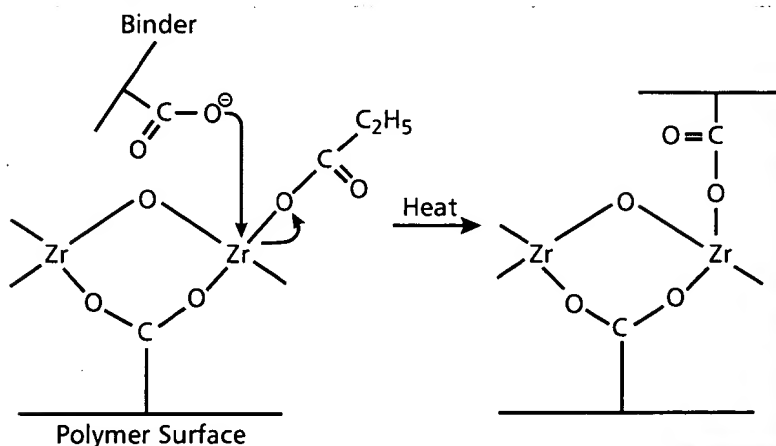
3. WATER BASED INKS AND PAINTS

Zirconium compounds in aqueous solution have the ability to crosslink carboxylated resins, and this ability can be used in both water based inks and paints to improve both heat resistance and scrub resistance. Some general work on the use of zirconium compounds to crosslink carboxylated resins will now be presented.

The crosslinking properties of zirconium compounds are made use of with a variety of resins. Carboxylated styrene acrylic co-polymers can be used with stabilised AZC (Bacote 20) to give films with high solvent resistance, as shown in Tables 1 and 2. The resistance to solvents and soap/water is marked, indicating a high level of crosslinking. These effects are now being commercially utilised.

Table 1.
Blank emulsion

		Solubility of dried emulsion film		
Drying Temp.	Drying time	Tetrachloro ethylene	Soap solution	Water
25C	24h	1h	1h	1h
80C	1h	1h	1h	1h
120C	5 min	1h	1h	1h

Table 2.
Effect on solubility of dried film through incorporation of Bacote 20 in emulsion

Level of Bacote 20 Added (%ZrO$_2$)	Drying temp	Solubility of dried emulsion film			
		Drying time	Tetrachlo- roethylene	Soap solution	Water
2	Room temp	24h	1 day	1 day	4 days
2	60°C	1h	1 day	4 days	4 days
2	120°C	5 min	1 day	4 days	4 days
4	Room temp	24h	1 day	1 day	4 days
1	60°C	1h	1 day	4 days	4 days
4	120°C	5 min	1 day	4 days	4 days

Zirconium crosslinkers have been compared to other crosslinkers and the results are extremely encouraging. (See Table 3.)

Acrylic emulsions have been investigated in some detail and these results are given in Table 4. Development work has shown that for acrylics in general, zirconium compounds tend to destabilise cationic or anionic stabilised systems (causing coagulation) but that stable solutions can be obtained with non-ionically stabilised systems.

Table 3.
Acrylic binder with various crosslinkers

Latex	% Pickup	Tensile strength		
		Dry	Wet	Wet/%Dry
Acrylic H	48.0	12.9	4.4	38.0
With 5%ZnNH$_4$CO$_3$	48.0	12.5	2.6	20.8
With 5% ZrNH$_4$CO$_3$	51%	13.7	4.5	33.0
With 5% WD Epoxy	50.8	10.6	4.7	44.4
With 2% Polyaziridine	49.2	14.3	6.7	46.9
None		4.6	1.4	30.5

Given suitable reactive groups in the acrylic, crosslinking can be induced by drying. Let us now consider a specific example. Zirconium acetate has shown strong interaction with a carboxylated emulsion (butylacrylate/methacrylate/acrylonitrile type containing 3% acrylic acid. In the initial work zirconium acetate was added to a non-ionically stabilised carboxylated emulsion and the resultant solution coated onto a plate, dried at 130°C for 30 minutes and a baked insolubles test performed using acetone as the solvent. The results are shown in Table 5.

As can be seen, baked insolubles are indicating a high degree of crosslinking. It is interesting to note that the baked insolubles increases at lower molar levels of zirconium. This has also been noticed in other work. It is believed that zirconium acts as a bridge via carboxyl groups, effectively increasing the molecular weight at lower Zr levels.

Table 4.
Solvent tensile results for acrylic binder without acrylonitrile and formaldehyde

	Tensile Strength					
	% Perchlor /Dry	Perchlor	% Heptane /Dry	Heptane	% MEK /Dry	MEK
Acrylic H	4.9	38.0	10.3	79.8	4.1	31.8
With 5% ZnNH$_4$CO$_3$	5.1	40.8	10.9	87.2	3.3	25.4
With 5% ZrNH$_4$CO$_3$	5.2	38.0	12.5	91.3	3.5	25.3
With 2% Polyaziridine	6.4	44.8	14.0	97.9	3.7	25.9
None	4.0	87.0	5.7	123.9	2.4	52.2

Table 5.
*Emulsion: Butylacetylate/methyacrylate/acrylonitrile containing 3% acrylic acid. Crosslinker: Zirconium acetate*

Molar ratio Zr:carboxyl groups	pH of system	Baked* insolubles
1:1	4.2	93.2
1:2	4.1	93.4
1:4	4.2	93.3
1:8	4.2	95.6
No additive	2.4	6.1

*Acetone used as solvent
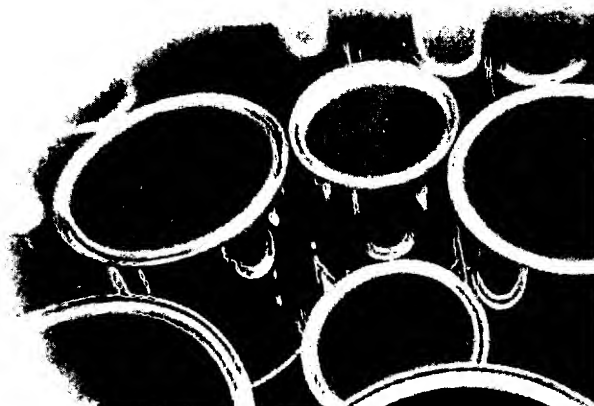
At higher levels of Zr, bridging is reduced by Zr polymers which are not linked to other carboxyl groups (i.e. carboxyl blocking rather than crosslinking). Obviously more polymeric zirconium species would give a more "open" structure and can lead to differences in properties. (See Fig 7.)

Fig 7. Modes of crosslinking

CROSSLINKING ACTION

BLOCKING ACTION (Crosslinking restricted)
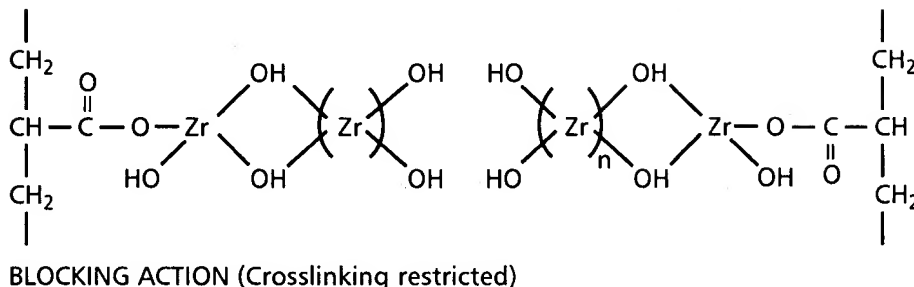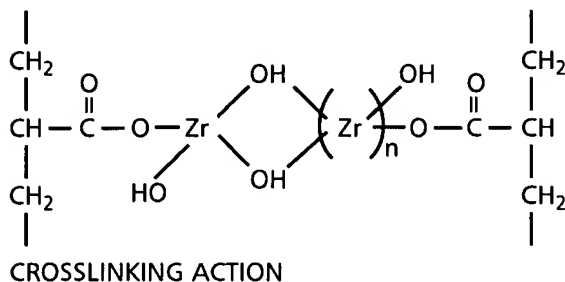
The pot life stability of these systems varies with the levels of Zr present.

Further work has investigated the effect of steric hindrance on the zirconium carboxyl interactions, and it has been shown that less sterically hindered carboxyl groups did not, after reaction with zirconium, give markedly better water resistance results. Hence the carboxyl groups should not be too well shielded such that reaction with the polynuclear zirconium is difficult but if it is not shielded enough, hydrolysis can occur. This again indicates the system can be tailor made for end user requirements.

Moving specifically to water based inks, ammonium zirconium carbonate can be used with a variety of commercially available resins to improve both heat and scrub resistance. A generalised formulation is:

Resin	50 parts
Water	50 parts
Titanium dioxide	20 parts
Ammonium zirconium Carbonate	0 - 6 parts

4. THE FUTURE

As will have been seen the ability of zirconium compounds to interact with carboxyl and hydroxyl groups leads to a whole range of new applications in surface coatings and these new applications will grow as demands on surface coatings become greater.

REFERENCES

1. A. Clearfield (1964), Rev. Pure Applied Chem.,
2. F. Farnworth. S.L. Jones and I. McAlpine (1981), In Speciality Inorganic Chemicals, R. Thomson, Ed., RSC, London, 165.